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Light-Mediated Manufacture and Manipulation of Actuators

Dong-Dong Han, Yong-Lai Zhang, Jia-Nan Ma, Yu-Qing Liu, Bing Han, and Hong-Bo Sun**

Recent years have seen a considerable growth of research interests in developing novel technologies that permit designable manufacture and controllable manipulation of actuators. Among various fabrication and driving strategies, light has emerged as an enabler to reach this end, contributing to the development of actuators. Several accessible light-mediated manufacturing technologies, such as ultraviolet (UV) lithography and direct laser writing (DLW), are summarized. A series of light-driven strategies including optical trapping, photochemical actuation, and photothermal actuation for controllable manipulation of actuators is introduced. Current challenges and future perspectives of this field are discussed. To generalize, light holds great promise for the development of actuators.

1. Introduction

Actuators are devices that can convert various forms of stimulations into mechanical deformation and perform mechanical work on the macro-,[1–3] micro-,[4,5] and nanoscale.[6,7] As a key component of robots, actuators have revealed great potential in various applications such as robotics, micromechanical systems (MEMS), adaptive optics, and biological/biomedical devices.[8–10] To make artificial devices smart, stimuli responsive materials (SRMs) and structures (SRSs) have been successfully developed over the past few decades. The former depends on the use of smart materials that have special response to surrounding environments (e.g., temperature, pH value, UV light or moisture), whereas the latter resorts to the construction of inhomogeneous multilayer structures which can lead to anisotropic motion under external stimulation.[11–15] Based on these SRMs/SRSs, actuators with distinguished properties of high sensitivity, intelligence, fast and reversible responses have been successfully manufactured with the help of various micronanofabrication technologies such as lithography, laser processing, imprinting and layer-by-layer assembly.[16] In addition to the manufacture technologies, novel driving techniques, for instance, electrostatic or piezoelectric actuation, magnetic remote control, optical tweezers, and pneumatic systems have been employed to manipulate actuators controllably.[17,18] For instance, magnetic micro-machines permit remote control using variable magnetic field.[19] Optical forces arised from the exchange of momentum between light and matter don't require novel materials or new kinds of light-matter interactions, they enable manipulation of a wide spectrum of objects, even nanoparticles.[20,21] Nowadays, the development of SRMs/SRSs also contributes to actuator driving. Without any external energy supply systems, actuators could be freely manipulated by changing the environmental stimulations.

Light plays a very important role in both manufacture and manipulation of actuators. From the view point of manufacturing, light-mediated fabrication such as UV lithography and DLW not only enables flexible design and processing of actuators profiles, even three-dimensional (3D) configuration, but also permits gradient tailoring or localized modification of the material properties, revealing great potential in the development of actuators.[22–25] For example, UV lithography allows designable patterning of photocurable SRMs, which makes it possible to fabricate self-folding devices;[26] femtosecond laser direct writing (FsLDW) is distinguished due to its real-3D farbication capability; 3D actuators based on pH sensitive hydrogel and proteins could be directly fabricated according to computer-designed models.[27] From the perspective of manipulation, light is a neat and safe energy source that could be transmitted to target objects through a noncontact manner. It is well known that optical trapping effects have been widely used for manipulating objects of different sizes. Additionally, remote control of actuators can be realized through various photochemical/photothermal mechanisms.[28–32] For instance, photoisomerization of azobenzene or spiropyran derivatitives, has been widely used for the development of photoactuators.[33–35] Making use of photothermal effects of a wide range of materials including carbon,[29,36,37] polymers[38] and metal nanoparticles,[39] light-driven actuators have been successfully developed based on photothermal expansion,[29] photothermal surface tension effect[40] and the photothermal phase transition.[41] Compared to other driving methods, light-driven actuators exhibit distinct advantages such as wireless/remote activation, spatial and temporal control, as well as localized manipulation rather than whole-field driven.[36–39] Moreover, light actuation permits exquisite control over various parameters such as the direction, wavelength, intensity and polarization of the incident light, emerging as a very promising driving manner.[42–44]

Here, we summarize the recent advances in both manufacture and manipulation of actuators using light. The general

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concept of light-mediated fabrication and manipulation has been illustrated in **Figure 1**. Several optical fabrication technologies including mainly UV lithography and DLW have been introduced, focusing on the manufacture of actuators. Then, various photo-driven strategies such as optical trapping, photochemical and photothermal actuation have been reviewed. Finally, we discussed the emerging trends and future perspective of this dynamic field. With the rapid progress of optical processing and driven technologies, light enabled actuators would find broad applications in many high-tech fields such as remote-control manipulator, unmanned flight, in vivo surgery and lab-on-a-chip systems.

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2. Light-Mediated Manufacture of Actuators

Light-mediated manufacture of actuators can be simply classified into two categories, UV lithography and DLW. UV lithography allows designable patterning; it has enabled a wide range of proof-of-concept devices, including various self-folding, origami and other complex deformable structures.[45] Moreover, UV irradiation also permits controllable tailoring of the property gradient of various materials along the lateral section, which makes it possible to fabricate actuators based on a solo material instead of multi-material layers.[22,46] In addition to UV lithography, DLW is another powerful tool for actuator manufacture. Particularly, FsLDW is capable of 3D fabrication in a programmable manner without the use of any masks. It makes it possible to "write" 3D actuators directly.[47]

2.1. UV Lithography

2.1.1. UV Lithography Patterning for Predictable Deformation

It is well known that UV lithography is capable of making designable micro-patterns on planar substrates. In the development of actuators, UV lithography plays a very important role in patterning both the profile and the key bending region of multilayer materials. With the help of UV lithography, actuators could perform predictable deformation due to locally changed thin-film stresses under various stimulations such as humidity,[1,46] solvents,[22,48] light,[49,50] temperature,[45,51] pH,[15,18] chemicals,[26,52] and even enzyme.[53,54]

As typical examples, Gracias's group successfully developed a series of "self-folding" actuators with the help of lithograph technologies. Toward a miniaturized mechanical surgeon under biocompatible conditions, they demonstrated multilayer μ-grippers with biopolymer hinges patterned using UV lithography. A key strategy that has emerged from this work is that multi-hinged μ-grippers can capture beads or cells from a tissue sample triggered by gelatin or carboxymethyl cellulose with high specificity to proteases or cellulases, respectively.[53] The stimuli-responsive hinge trigger could be patterned atop the grippers to control actuation. With the reduced dimensions, they can readily capture individual red blood cells and mouse fibroblast cells.[10] Self-folding/unfolding devices hold great promise for applications in biochemicals encapsulating, drug releasing and even self-propellings.[26,51] The idea is not limited to this special case, under a similar design principle; UV lithography patterning has been applied to divers actuator models including a pyramidal structure,[48] a six-sided closed box,[49] and "teardrop" state of the twelve-lane polymer actuator.[50]

In addition to simple self-folding actuators, UV lithography patterning also helps to achieve more complex deformation providing new fabrication methods and design principles could be developed. Recently, Hayward et al., reported a simple approach to fabricate reversibly self-folding origami based on trilayer films of photocrosslinkable copolymers.[45] It is well known that the essential characteristics of origami are a pattern of creases including both valley and mountain folds. In their work, a thermally responsive hydrogel layer is sandwiched by two patterned thin rigid polymer layers. The UV lithography patterning helps to form open stripes of defined width in the top and bottom poly(p-methylstyrene) layers (different patterns), such that controllable valley and mountain folds could be achieved when the thermally responsive hydrogel layer (the interlayer) swells (**Figure 2**). Besides, the same group successfully developed a halftone gel lithography method using only two photomasks, wherein highly cross-linked dots embedded in a lightly cross-linked matrix formed based on poly(N-isopropylacrylamide) copolymers containing pendent benzophenone

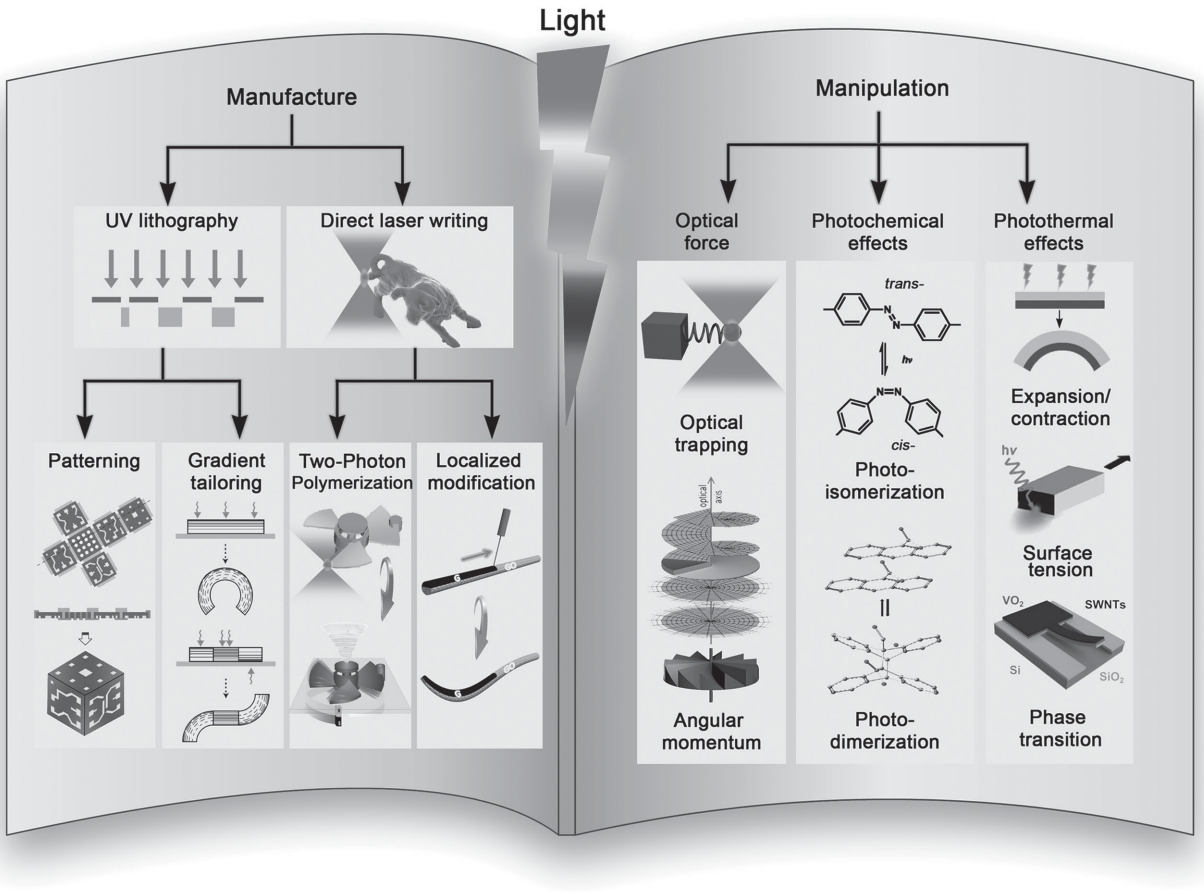

Figure 1. General concept of light-mediated manufacture and manipulation of actuators. Reproduced with permission.[3] Copyright 2014, Nature Publishing Group;[19] Copyright 2010, Wiley-VCH.[22] Copyright 2015, American Chemical Society;[24] Copyright 2013, Wiley-VCH;[25] Copyright 2011, Wiley-VCH;[40] Copyright 2009, American Chemical Society[44] Copyright 2015, American Chemical Society;[78] Copyright 2014, Nature Publishing Group;[80] Copyright 2012, American Institute of Physics;[91] Copyright 2009, American Chemical Society.

units.[13,55] In this way, temperature-responsive gel sheets that can transform between a flat state and a prescribed 3D shape have been realized.

In the manufacture of actuators, UV lithography patterning exhibits a series of advantages: (i) designable patterns could be fabricated for predictable deformation; (ii) complex 3D deformation could be realized using simple two-dimensional (2D) structures; (iii) actuation could be tuned by patterning different materials. Meanwhile, UV lithography also suffers from serious drawbacks. For instance, UV lithography is limited to photopolymers. Moreover, the 2D processing feature restricts its application in 3D structuring or on non-planar substrates.

2.1.2. UV Irradiation for Material Property Gradient Tailoring

In addition to designable patterning, UV irradiation also enables controllable tailoring of material property gradient along lateral dimensions, providing an alternative way to make material smart. The responsive mechanism is similar with that of multilayer materials. When material property gradient along lateral dimensions has been continuously altered, the resultant material would exhibit asymmetric response to ambient environment, and could be manipulated under certain stimulation. There exist several successful examples of actuators prepared in this way. For instance, UV irradiation allows precise control over the cross-linking gradients along the thickness. As reported by Gracias et al.,[22,56] heterogeneous SU-8 films that show different swelling ratios in different solvents (e.g., acetone or water) have been well developed by progressively less exposure along the thickness of the films. Through multiple photolithographic patterning of the differentially photocrosslink SU-8 films from above and below, it enables to create flower-shaped structures, cylinders, cubes, and bidirectionally folded sheets.

In addition to cross-linking gradients, Kamal et al., have further developed an asymmetric porous gradient structure along the thickness direction through UV treatment.[48,52] Due to the limited penetrability of UV-light into the mixture of polymer precursor, an asymmetric polymer film with different porous structure would form. The UV-exposed surfaces were pore-free and compact, whereas the opposite surface was highly porous. The mechanisms should be attributed to the competition between polymerization and phase-separation; and the difference in swelling leads to curling behavior when being immersed in solvents.

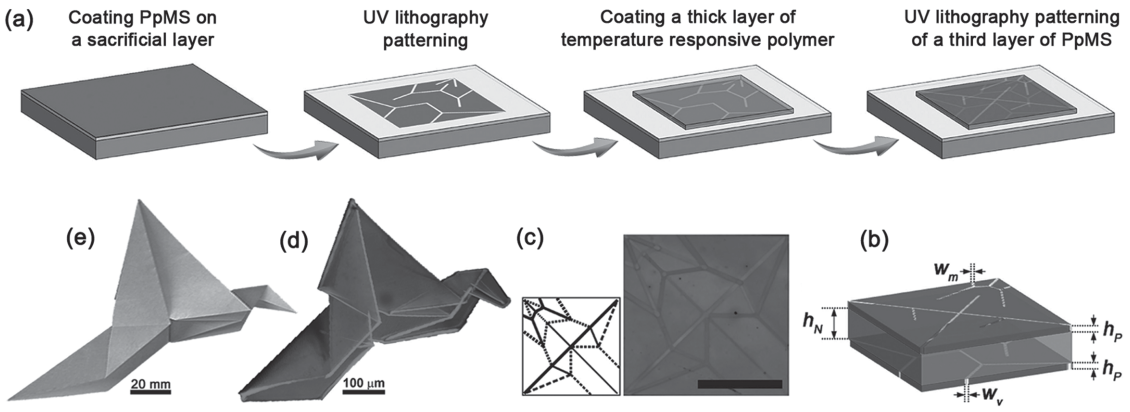

Figure 2. a) Schematic illustration of the fabrication of the folded Randlett's flapping bird. A thin layer of a photo-crosslinkable glassy polymer on a substrate with a sacrificial layer is photolithographically patterned with open stripes to define the positions and angles of the valley folds. Then, a thicker layer of temperature-responsive polymer is coated on top and uniformly crosslinked over the entire area. Finally, a third layer of glassy polymer is coated and patterned with open stripes to define the positions and angles of the mountain folds.b) A magnified schematic of the resulting tri-layer film. c) An optical image (scale bar: 400 μm) and d) alongside a fluorescence image of the self-folded tri-layer film patterned to fold into Randlett's flapping bird. e) The folded Randlett's flapping bird using paper. Reproduced with permission.[45] Copyright 2015, Wiley-VCH.

The UV irradiation mediated gradient tailoring is not limited to photopolymers, our group tuned the oxygen containing groups (OCGs) gradient along the lateral direction of graphene oxide (GO) paper through a self-controlled UV photoreduction treatment, and successfully fabricated graphene-based moisture responsive actuators (**Figure 3**a).[46] Due to the limited light transmittance and thermal relaxation, thick GO paper could not be fully reduced under UV irradiation from one side. Thus a GO/reduced GO (GO/RGO) bilayer structure with gradually changed OCGs distributions has been prepared (Figure 3b). Interestingly, the unilateral photoreduction significantly alters the water adsorption capabilities of the RGO side, which endows sensitive moisture responsive property to the GO/RGO bilayer paper (Figure 3c). Accordingly, actuators including a claw, an orientable transporter, and a crawler paper robot have been demonstrated.[1] After that, a graphene "tendril" actuator has been fabricated by combining UV lithography patterning and gradient tailoring. It can twine round objects under high humidity and release them in dry air.

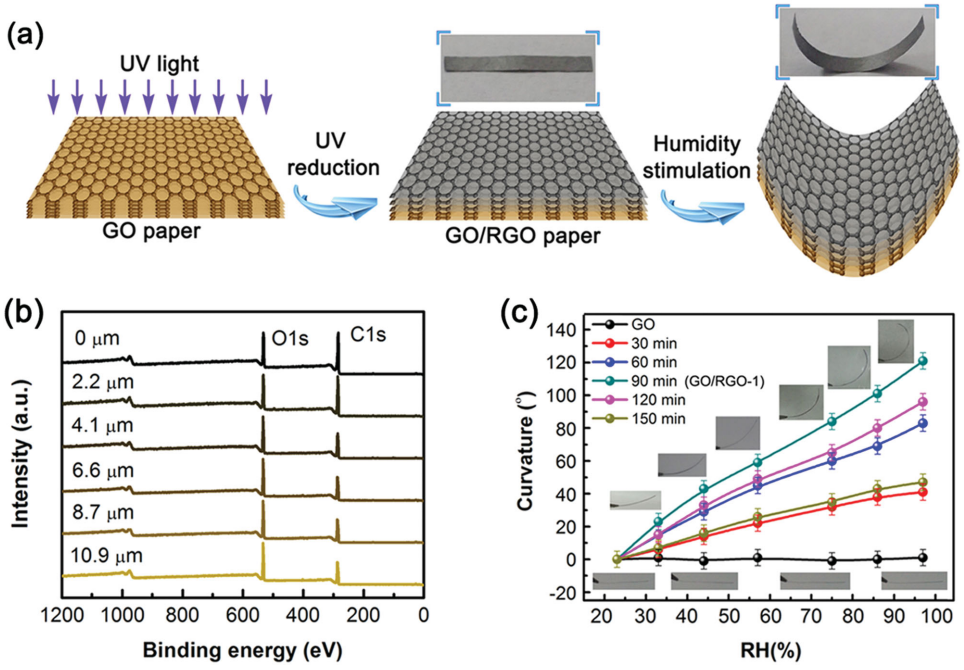

Figure 3. a) Schematic illustration of the UV irradiation tailoring of OCGs gradient along the lateral direction of a GO paper. b) Survey XPS spectra of smart GO/RGO paper revealed an upward trend in oxygen and a downward trend in carbon signals with different depth. c) The dependence of bending performance on relative humidity of smart GO/RGO paper. Reproduced with permission.[46] Copyright 2015, Wiley-VCH.

As an alternative to multi-materials deposition, gradient tailoring of material/structural properties provides another approach to prepare stimuli responsive structures based on a solo material. As compared with multilayer materials, UV gradient tailoring allows continuously tuning of material properties. Moreover, the problems with respect to interlayer adhesion in the multilayer materials would be avoided in the case of solo material; accordingly, the stability of this kind of actuators would be improved.

2.2. Direct Laser Writing

In addition to UV lithography that deals with 2D micro-patterns, DLW technology, especially FsLDW, is capable of processing 3D micro/nanostructures,[47] providing an avenue to manufacture 3D actuators. Recently, the spatial resolution of FsLDW has been significantly improved to tens of nanometers; and processible materials have been extended to a broad range, for instance, photopolymers,[19,57] protein,[8,23,27] hydrogel,[58] carbon,[59,60] metal,[61] and even nanoparticles,[62] etc. The rapid progress of FsLDW technology also contributes to the advances of actuators. In this section, we briefly summarized the recent development in DLW mediated manufacture of actuators.

2.2.1. FsLDW Based on SRMs

It is well known that FsLDW has been widely used for 3D processing of photopolymers through two-photon/multi-photon absorption. To make general photopolymers "smart", doping or post-deposition of functional materials provides a way to fabricate actuators. As typical examples, Xia et al., prepared a photosensitive ferrofluid that consists of general photopolymers and Fe_3O_4 nanoparticles for designable fabrication of remotely controllable 3D micro-machines;[19] The as-fabricated micro-turbine could be used for microfluids mixing. Later, Zhang et al., fabricated the helical swimming micro-machines based on SU-8 or IP-L by DLW.[57] After the deposition of Ni/Ti thin bilayers on the surface, the helical micro-machine could be manipulated by magnetic field, and performs steerable cork-screw motion as well as transportation procedure.

Alternatively, FsLDW based on SRMs, for instance, hydrogel and protein, has also been reported for the development of actuators. Sun et al., fabricated pH-responsive protein micro/nanoarchitectures by FsLDW (**Figure 4**a).[27] Since the photo-cross-linked bovine serum albumin (BSA) structures contain weak acidic and weak basic pendant groups that become protonated or deprotonated as the pH value varies, the resultant BSA actuators could be manipulated by controlling the electrostatic interaction. As shown in Figure 4b, 3D relief portrait of a face swelled to about 150% within seconds when the pH value was increased from pH 7 to pH 13. Importantly, the surface of the as-prepared protein microstructures is so smooth that it could be further used for tunable optical devices. The focal length of a micro-lens can be continuously and dynamically tuned by changing pH value (Figure 4c). Besides, Lee et al., developed 3D shape-changing microstructures (10–30 μm) based on a single material BSA; various actuators including dual-pillar

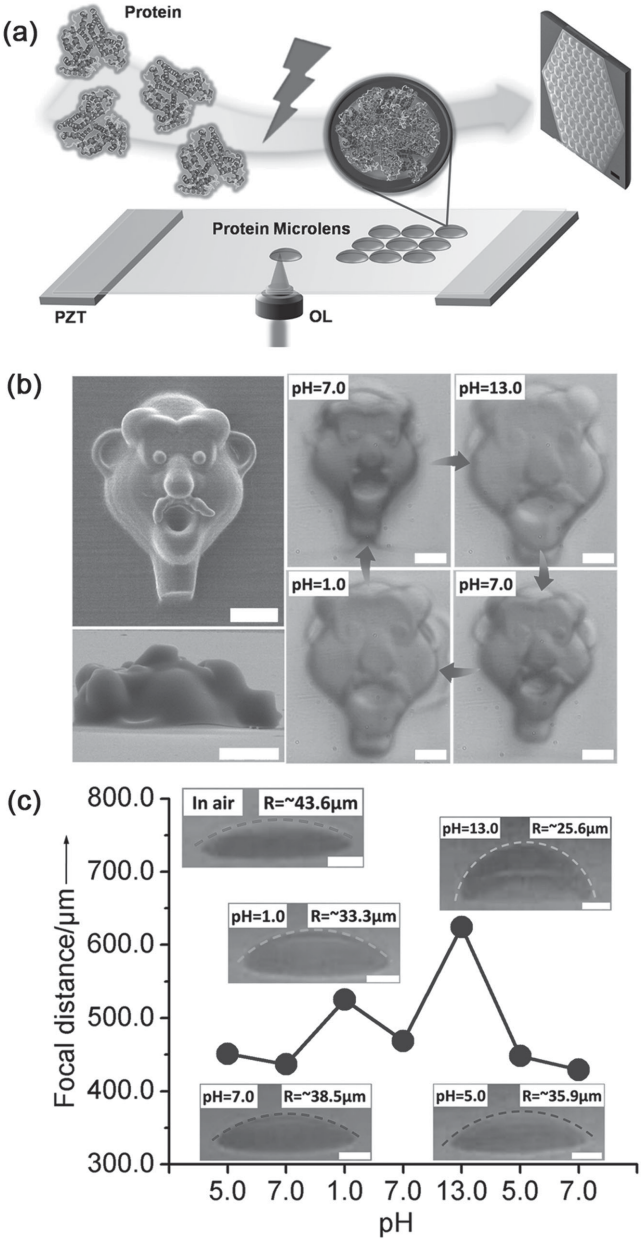

Figure 4. a) Schematic illustration of the FsLDW fabrication of protein microarchitectures. b) Vertical and lateral SEM pictures of a 3D relief of a face (left) and reversible deformation of the microstructure induced by changing the pH value (right). Scale bar: 10 μm. c) Focal distance versus pH value of a protein microlens. Reproduced with permission.[27] Copyright 2012, Wiley-VCH.

"Y" shaped structures, dual-pillar cross-shaped structures, and "l" shape dual-pillar structures undergo a shape change to chiral/reverse "S" structures, μ-trap which is able to open and close in response to a pH change, have been successfully fabricated.[63] Due to the excellent biocompatibility, protein based actuators hold great promise for applications in bio-chips.

In addition to protein, photo-crosslinkable hydrogel and polymers are also workable for design and manufacture of actuators. For instance, Tian et al., fabricated solvents responsive

micro-machines by FsLDW of methacrylate-based photoresist;[64] Lu et al., integrated tunable polydimethylsiloxane (PDMS) micro-lenses within a microfluidic channel by the FsLDW.[65] As compared with traditional 2D micro/nanofabrication technologies, FsLDW shows a series of distinct advantages. For instance, it enables programmable 3D fabrication without the use of any shadow masks; the spatial resolution has been improved to nanoscale; and FsLDW is suitable for a wide range of materials.

2.2.2. Localized Modification for Actuation

As mentioned above, direct processing of SRMs enables fabrication of smart structures that possess isotropic response to environment change. To realize more complex deformation, DLW technology has also been employed to fabricate asymmetric structures through localized modification. In our previous work, we demonstrated FsLDW induced reduction and patterning of GO.[60] Since FsLDW treatment could significantly alter the water adsorption ability of GO, region-selective reduction of GO provides an opportunity for design and manufacture of the graphene-based actuators. For example, Qu et al., designed and fabricated an asymmetric graphene/graphene oxide (G/GO) fiber by FsLDW induced local modification of a GO fiber (**Figure 5**a-c).[24] The asymmetric G/GO fiber can bend to the graphene side once exposed to moisture. As shown in Figure 5d–k, by localized laser reduction of GO fiber at different position of the GO fiber, sophisticated shape changes including a folded, hook, S-shaped, and self-supporting spring structures, can be achieved when being exposed to moisture (RH = 80%).

Actually, the essence of fabricating deformable materials lies in the formation of asymmetric structures, DLW induced localized modification provides an effective manner to alter material properties at any desired positions of various materials, revealing huge potential in the development of actuators. In addition to the modification of one-dimensional GO fiber, DLW induced localized modification would be extended to more complex 3D structures. For example, with the rapid progress of 3D printing technology, it may emerge as an enabler to transform general sculptures to smart robots. To make an overview of light-mediated manufacture of actuators, typical works have been summarized in **Table 1**.

3. Manipulation of Actuators Using Light

In addition to the manufacture, light is also capable of manipulating actuators. In this section, light manipulation has been classified into three categories, including optical force, photochemical effect and photothermal effect actuation. Optical force actuation relies on the direct momentum transfer from radiation to matter; it can convert optical power into mechanical work.[7,66,67] Photochemical effects, such as photoisomerization and photodimerization, make full use of various photoreactions of light-sensitive groups;[68–70] whereas photothermal effects resort to light-to-heat conversion, including photothermal effect induced expansion/contraction, absorption/desorption and phase transition.[28,29,41,71]

3.1. Optical Force Manipulation

When a focused laser beam irradiates an object, optical forces arise from the exchange of momentum between light and matter according to the law of conservation of momentum.[66] Making use of the light-matter interaction, optical force could be directly used for trapping, moving, fixing and rotating

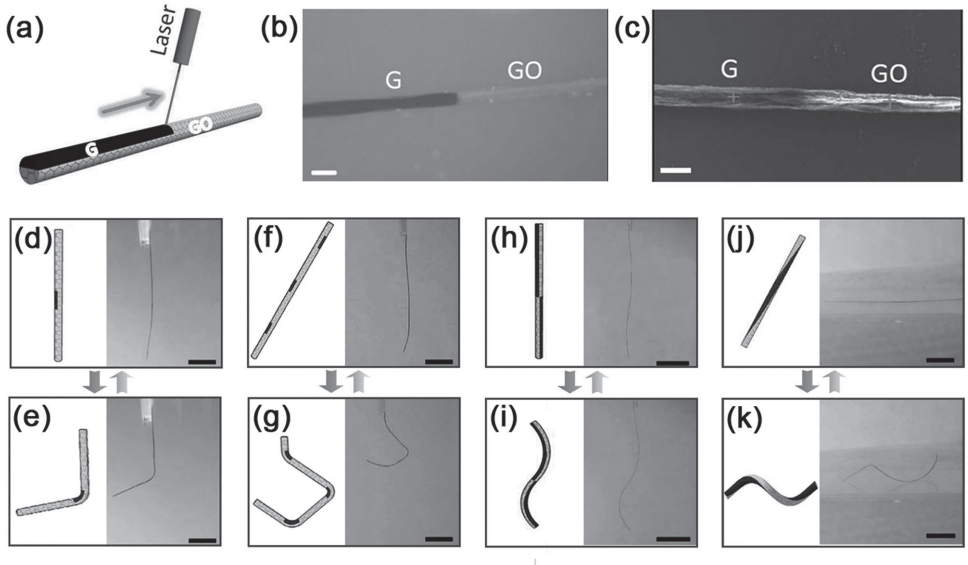

Figure 5. a) Representation of the laser local reduction of a GO fiber. Photomicrograph (b) and SEM image (c) of the top surface of the as-prepared asymmetric G/GO fiber. Scale bars: 50 μm. d–k) Schematic diagrams and photographs of different G/GO fibers and their reversible deformations with changes in humidity at RH = 80%. Scale bars: in (d,e,j,k): 5 mm; in (f,g,h,i): 1 cm. Reproduced with permission.[24] Copyright 2013, Wiley-VCH.

Table 1. Typical examples of light-mediated manufacture of actuators.

Technology	Advantages	Processible Materials	Stimulations	Response/motion	Ref
UV-lithography	Patterning	Biopolymer	Enzyme	Bending/folding	[53]
		LC polymer[a)]	Temperature, pH, IR	Bending/folding/twisting	[50]
		Photopolymer	Temperature	Curving/bending/folding	[13,45,51]
	Gradient control	Photopolymer	Acetone/water	Curving/folding	[22]
		LC polymer	Acetone/water	Bending/helical twisting	[48]
		GO	Humidity	Bending/helical twisting	[46]
DLW	3D structuring	Ferrofluids	Magnetic field	μ-spring/μ-turbine	[19]
		Photopolymer	Magnetic field	Helical swimming	[57]
		Protein	pH	μ-lenses/bending/3D deformation	[27,63]
		PBMA[b)]	Solvent	μ-wire/shrinking	[64]
		PDMS	Solvent	μ-lens tunable focal length	[65]
	Localized modification	GO	Humidity	Bending/hook/S-shape/spring	[24]

[a)]Liquid crystal polymer; [b)]Poly-butylmethacrylate.

microstructures. The concept of optical trapping had been reported as early as 1970.[72] It is a well-known phenomenon that doesn't require novel SRMs or SRSs, so it seems that optical force manipulation does not fall in the scope of "actuator". However, considering the fact that optical tweezers contribute greatly to the manipulation of micro-objects,[7,73] optical force manipulation has been briefly introduced.

Generally, optical force could be decomposed into the scattering force, which is in the direction of the laser beam; and the gradient force that always points to the laser focus. For stable trapping, the gradient force must overcome the scattering forces which point down the beam axis. To address this problem, one can use either a tightly focused laser beam with the help of a high-numerical aperture (NA) microscope objective or counter-propagating beams in the case of low-NA microscope objective to achieve stable trapping.[21,74] For singe-beam trapping, the optical trapping regimes can be described using different models that depend on the particle's size (r, radius) in relation to the light wavelength (λ): (i) if the particle is much smaller than the wavelength ($r << \lambda$), it is usually called Rayleigh regime, the electromagnetic model could be used to better understand the trapping mechanism. In this case the force scales as the cube of the particle's radius; (ii) if the particle size is much larger than the wavelength ($r >> \lambda$), it is referred to as Ray optics regime or geometric optics regime, in which ray optics can be used, and the trapping force is independent of particle size; (iii) if the particle size is comparable to the wavelength ($r \approx \lambda$), Mie-scattering theory helps to bridge this gap between the two regimes.[75,76] In addition, to create large numbers of high-quality optical traps in arbitrary 3D configurations, optical tweezers can be combined with digital holography, in that case, real-time 3D manipulation of multiple particles could be realized.[77]

Beyond the manipulation of colloidal particles, optical tweezers also hold great promise for driving micro-machines in a non-contact manner. For instance, Kawata et al., reported the operation of a micro-oscillator by using laser trapping force (**Figure 6**a,b).[78] In their work, sophisticated operation of the micro-oscillator, such as the capture of the bead, the pulling of the spring, and its release from its displacement, could be easily realized. Besides micro-objects, optical trapping is also workable to nanoparticles. In the case of Rayleigh regime, the force scales as the cube of the particle's radius; the gradient forces gain rapidly in significance as the particle size decreases.[76] Consequently, gradient force accounts for the trapping of nanostructures in most cases. Optical trapping at nanoscale may open unprecedented opportunities in ultra-accurate manipulation of nano-robots.[20,21]

It is well known that light carries both linear and angular momentum; the angular momentum of light can also be used for optical manipulation.[79] To actually use the spin angular momentum to rotate particles, Wu et al., reported laser-driven spinning birefringent spheres to direct nerve fibre growth.[4] Circularly polarized light with angular momentum could cause the trapped bead to spin. In this way, a localized microfluidic flow would be created, which generates an estimated 0.17 pN shear force against the growth cone that turns in response to the shear. The direction of axonal growth can be precisely manipulated by changing the rotation direction and position of the micro-motor. In addition to spin angular momentum, orbital angular momentum has also been adopted for actuation.[20,79] Lin et al., developed a light driven turbine-like symmetric micro-rotor using two-photon polymerization (TPP).[80] As shown in Figure 6c, light derived from a spiral phase plate (SPP) that can be converted into a helical wave. When a plane wave passes through a SPP, it could be converted into a helical wave that carries orbital angular momentum. Meanwhile, it gives the SPP an inverse angular momentum that could exert a torque to actuate a rotation of the SPP. According to this basic principle, a symmetric micro-rotor was rationally designed and fabricated by TPP (Figure 6d–f). It could rotate at a rate over 500 r min^{-1} with average orbital angular momentum transfer up to 34.55 $\hbar$ $photon^{-1}$. The light driven micro-rotor is a useful telecontrolled device free of mechanical contact.

Both the optical trapping and the angular momentum of light tremendously devoted a series of unique advantages to

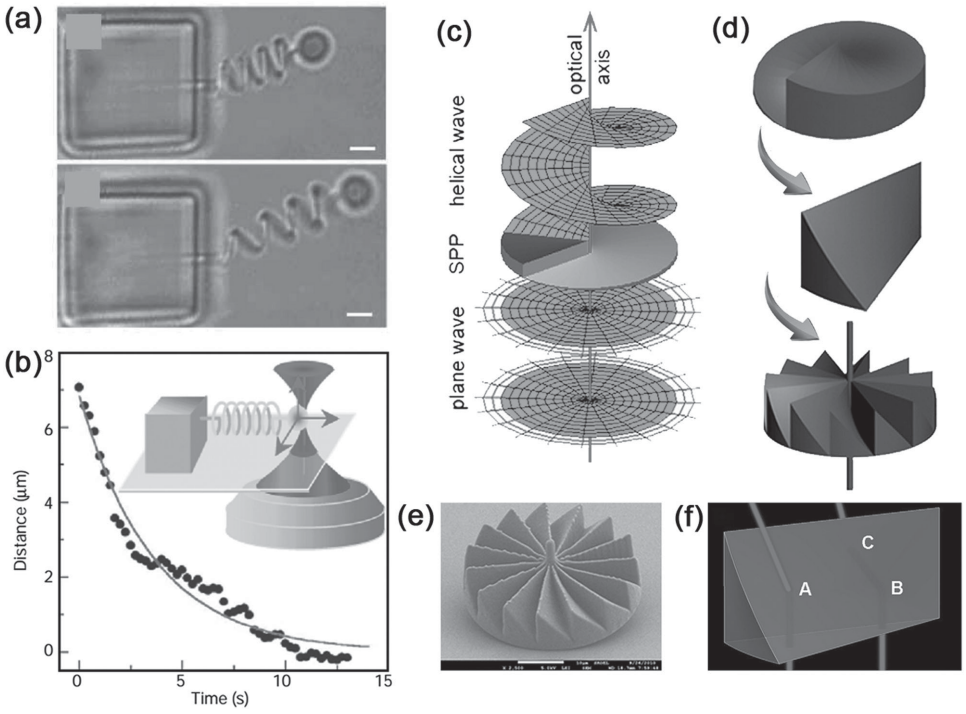

Figure 6. a) SEM images of a functional micro-oscillator system fabricated by FsLDW. Scale bars, 2 μm. b) Restoring curve of the damping oscillation; inset, diagram showing driving of the oscillator by using laser trapping. The spring constant was deduced to be 8.2 nN m^{-1}. Reproduced with permission.[78] Copyright 2001, Nature Publishing Group. c) A SPP converting a plane wave into a helical wave. d) Design of a turbine-like micro-rotor. e) The SEM image of the fabricated micro-rotor. f) Schematic diagram of the driving mechanism. Reproduced with permission.[80] Copyright 2012, American Institute of Physics.

the manipulation of micro-devices, for instance, non-contact manipulation and precise control. However, optical force manipulation of large particles in liquid media may suffer from a much higher drag from the fluid, and therefore the dynamical effect of the forces is much less pronounced. In this regard, continued developments in optical driving, such as plasmon-enhanced forces, will likely improve this situation and may give possibilities for more applications in diverse areas.

3.2. Photochemical Manipulation

Recently, some review articles published elsewhere have summarized the development of photo-actuators based on photochemical stimulations, in which photo-responsive polymers that can undergo a change in molecular properties in response to a light stimulus are crucial.[34,35,81,82] By integrating the photosensitive chromophores in different polymers and crystals, the mechanical motions (e.g., bending and curling) of the resultant materials could be manipulated in a reversible, dynamic fashion.[33,42,83] Over the past decades, a wide range of light-sensitive molecules have been prepared for photo-actuation, for instance azobenzenes,[11,84,85] diarylethenes,[86–88] anthracene derivatives,[69,89–91] salicylideneaniline analog,[92] spiropyran derivatitives,[93,94] and other alkenes.[95] On the basis of these photosensitive materials, controllable manipulation through various photochemical reactions, such as photoisomerization and photodimerization, has been successfully realized.

3.2.1. Photoisomerization

To make a polymer photosensitive, photochromic dyes are usually incorporated in the polymer network.[96] In this way, photoisomerization (e.g., E/Z isomerization, valence isomerization, cycloaddition and tautomerization) could be used for photo-actuation.[97] As a commonly used dye, spiropyran derivatitives which can isomerise into hydrophilic merocyanine have been well investigated for the development of both photoresponsive coatings and photo-actuators.[94] For instance, the incorporation of spiropyran in N-isopropylacrylamide (NIPAAM) polymers in slightly acidic media has led to the development of smart photoresponsive hydrogels. The stable hydrophilic isomer merocyanine-H^+ (McH^+) can be switched to the ring-closed hydrophobic spiropyran form upon light irradiation, allowing reversible swelling and shrinkage of the material, due to water uptake and release.[35] Spiropyran and its derivatitives are quite unique among various photoresponsive polymers, since the two isomers have vastly different properties. However, in order to use this kind of "smart materials" in actuators, it is necessary to covalently attach the spiropyran units to certain support, for instance, hydrogel networks.

Another important light-sensitive molecule would be azobenzene and its related materials.[11,68] Generally, azobenzene isomerizes from a rod-like trans state to a bent cis configuration upon UV irradiation; it returns to the trans state when irradiated by visible light, heated or absorbed water.[84,98,99] Since the trans state of the molecule would align with the mesogenic host

material, whereas the bent cis state would decrease the order of the mesogenic host, the trans-cis photoisomerization can be effectively used to cause a shape change.[70,85] According to this principle, Ikeda's group firstly reported light induced bending of a single film of liquid-crystal (LC) network containing azobenzene chromophore. A 366nm linearly polarized light was used as stimulus, because the photoisomerization generates a surface volume contraction parallel to the polarization direction.[33] Furthermore, they prepared crosslinked liquid-crystalline polymers (CLCPs) fibers with an azobenzene moiety for 3D actuation.[100] In their following studies, photoisomerization has been widely employed for various actuation such as rolling, robotic arm, inchworm walker, and a light driven plastic motor.[101] Photoisomerization mediated actuation is not limited to simple bending, by rational deign of device structures, photoactuators such as azo dye-doped liquid-crystal elastomers (LCEs) swimmer,[68] photomechanical device in optical systems,[102] cantilever oscillators,[103] optical pendulum generator,[104] voltage divider,[70] robot arm,[105] microrobot picking-lifting-moving,[106] microvalves,[107] spoke-type micromotor,[108] gripper,[98] nanowire tweezers,[109] have been successfully developed.

To realize more complex performance, Iamsaard et al., presented a variety of chiral twisting motions by adding the chiral dopant (S-811 or R-811) to the chiral liquid crystals.[3] Interestingly, their photoresponsive behavior, including helix tightening, helix unwinding and stretching, is related to different cuts direction of ribbon. Besides, mixed-helicity springs, which comprise two oppositely handed helices joined at a kink, displayed a "push-pull" mechanism by alternating irradiation cycles of UV and visible light (**Figure 7**a–d). Additionally, Oosten et al., created artificial cilia by inkjet printing technology with two different dyes (A3MA and DR1A) in different part of the structures.[30] The A3MA and DR1A had trans absorption

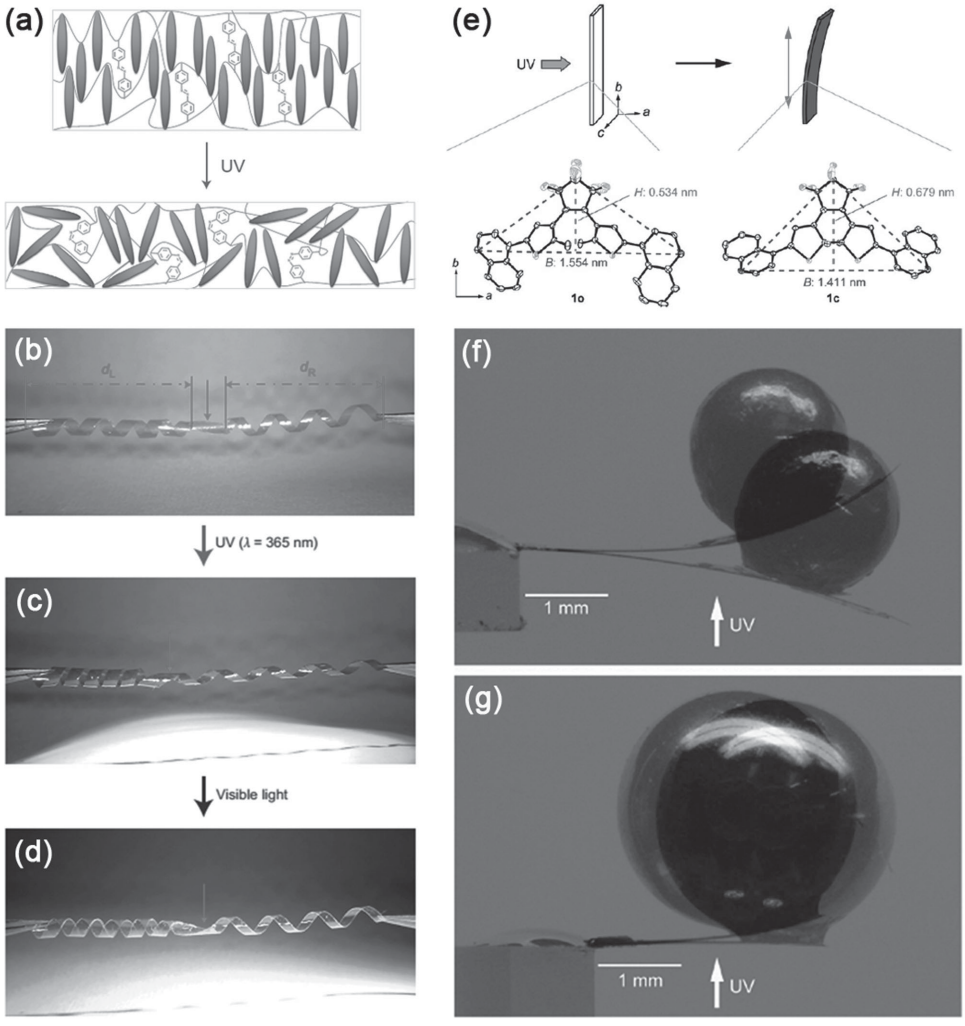

Figure 7. a) Photoactuation modes of the polymer springs doped with chiral dopants. Under UV irradiation, the ribbons contract along the director and expand in the perpendicular directions. b–d) The mixed-helicity ribbon performs a piston-like motion irradiated alternately with ultraviolet and visible light. Reproduced with permission.[3] Copyright 2014, Nature Publishing Group. e) Schematic illustration of the photoinduced bending. The left is open-ring isomer in the cocrystal, and right is closed-ring isomer in the crystal. Hydrogen atoms were omitted for clarity. f,g)The crystal cantilever can lift a steel ball before and after irradiation with UV (365 nm) light. Reproduced with permission.[88] Copyright 2010, American Chemical Society.

peaks centered at 358 nm and 490 nm, respectively. Therefore, the cilia-like actuator allows fitting into four positions by selecting the wavelength of driving light.

It is worthy pointing out that azobenzenes and their related materials are very popular for photoactuators due to the distinct advantages including ease of synthesis and good miscibility with many liquid-crystalline molecules. However, they also suffer from several problems, for instance, to avoid the thermal trans-cis isomerization, the photoactuators are often workable at room temperature; the poor biocompatibility and non-biodegradable properties to some extent limit their in vivo applications.

In the case of open-closed ring isomerization, a typically used light-sensitive molecule is diarylethenes. Compared with azobenzene, diarylethene has better thermal stability because they are crystals. Generally, photochromic reactions rarely occur in crystals, since large geometrical structure change is usually prohibited. However, many diarylethene derivatives permit photochromism even in the crystalline phase, because the geometrical structure change of diarylethene derivatives during the photochromic reactions is relative small as compared with azobenzene and spiropyran derivatives.[12] It is well known that molecular crystals are densely packed and organized systems; the shrinking/expansion of a diarylethene molecule through the ring-closing and ring-opening reaction upon UV and visible light irradiation, respectively, would undoubtedly lead to obvious shape deformation of the bulky crystal.[82] In this way, macroscopic mechanical movement of materials based on molecular-scale structure changes of individual molecules could be realized in molecular crystals of diarylethene derivatives. Irie and co-workers have studied several diarylethenes that display a fascinating photoresponse upon UV irradiation.[12] The rectangular plate-like cocrystal was fixed at the edge of a glass plate as a cantilever arm, which could lift a lead ball as high as 0.95 mm upon UV irradiation; the amount of the work is as large as 0.43 μJ (Figure 7e–g).[88] On the basis of this design principle, such actuating crystals can perform desired works by rotating gears,[87] or act as electrical circuit switch.[110]

The photoisomeization actuation kinetics depends on both intrinsic factors,[99,104,109,111] such as the thickness, crosslinking density, aspect ratio, initial alignment of mesogens, concentration of photoactive chromophores, microparticle-enhanced photoresponse, and external factors,[43,102,105,112] for instance, excitation time, direction, intensity, the light polarization, and the temperature. So there exists a large space to tune the responsive properties of photoactuators based on photoisomerization. Meanwhile, the photoinduced bending performance can be trigged by various light source, such as blue light (405 nm, 420 nm),[113] blue-green light (440–514 nm),[114] red light (635 nm),[115] near-IR light (980 nm),[116] or even sunlight,[117] which makes photoisomerization a universally applicable driving strategy. Additionally, to further enhance the mechanical properties of these photoactuators, divers modification strategies such as hydrogen bond crosslinking,[118] electrostatic interaction,[119] incorporation of the poly-alkyl methacrylate,[120] and aligned carbon nanotube (CNT) sheets,[121] have been successfully employed to the photoactuators based on photoisomerization.

3.2.2. Photodimerization and Others

In addition to photoisomerization, photodimerization is another photochemical strategy for photoactuation. Bardeen et al., reported photoactuators based on anthracene derivatives that undergo an intermolecular photodimerization to form a bridged photodimer upon irradiation.[89] They found that molecular crystal nanorods composed of 9-anthracene carboxylic acid (9-AC) can undergo reversible photoinduced cycling between well-defined shapes after spatially localized excitation in aqueous solution.[90] The kinetics of recovery depends on illumination conditions. Subsequently, they used a modified floating-drop method to grow oriented crystal microribbons demonstrated reversible photoinduced twisting.[91] In their recent results, they found that crystal morphology and reaction dynamics progress affect photomechanical deformations of single microcrystals.[69]

Besides, there are several other photochemical strategies that could be used for photoactuation. For instance, Techawanitchai et al., integrated *o*-nitrobenzaldehyde (NBA) into two pH-responsive hydrogel layers to induce proton-releasing reaction upon UV irradiation.[14] Xiao et al., reported the photochemical Marangoni effect to produce photoresponsive ON-OFF-ON motion of a macroscopic object on water surfaces.[42] In these pioneering works, the driving force for the deformation is suggested to arise from the photoreactions. Examples of the initial strategy were limited to potentially damaging ultraviolet wavelengths; with the development of more photoresponsive materials, light sources throughout a broad spectral range might become workable.

3.3. Photothermal Manipulation

Photothermal effect has been widely employed in actuators, since there are various photosensitive materials that can convert light into heat. For example, carbon materials,[29,31,36,37,122] noble metal nanoparticles,[39] metal complexes,[44,123] and photothermal polymers[38] are typical photothermal materials that could be used for actuation. In this section, we simply classified the photothermal strategies into three categories: (i) photothermal expansion/contraction, (ii) photothermal effect induced surface tension gradient, and (iii) photothermal effects induced phase transition.

3.3.1. Photothermal Induced Expansion/Contraction

Photothermal effect induced expansion/contraction is a general mechanism for multilayer photoactuators. Due to mismatches in thermal expansion coefficients between different layers, the photothermal effects would directly lead to obvious deformation upon light irradiation. Taking advantage of the photothermal properties of single wall carbon nanotubes (SWNTs), Zhang et al., exploited a simple, facile and scalable method to fabricate reversible, thermally- and optically responsive polymer/SWNT bilayers actuators by vacuum filtration of a SWNT solution on a 10-μm-thick polycarbonate (PC) membrane.[29] The SWNT layer absorbs light with high efficiency, allowing the temperature of the substrate increased by ≈20 °C under 100mW cm^{-2} illumination (**Figure 8**a). Since the thermal expansion coefficient

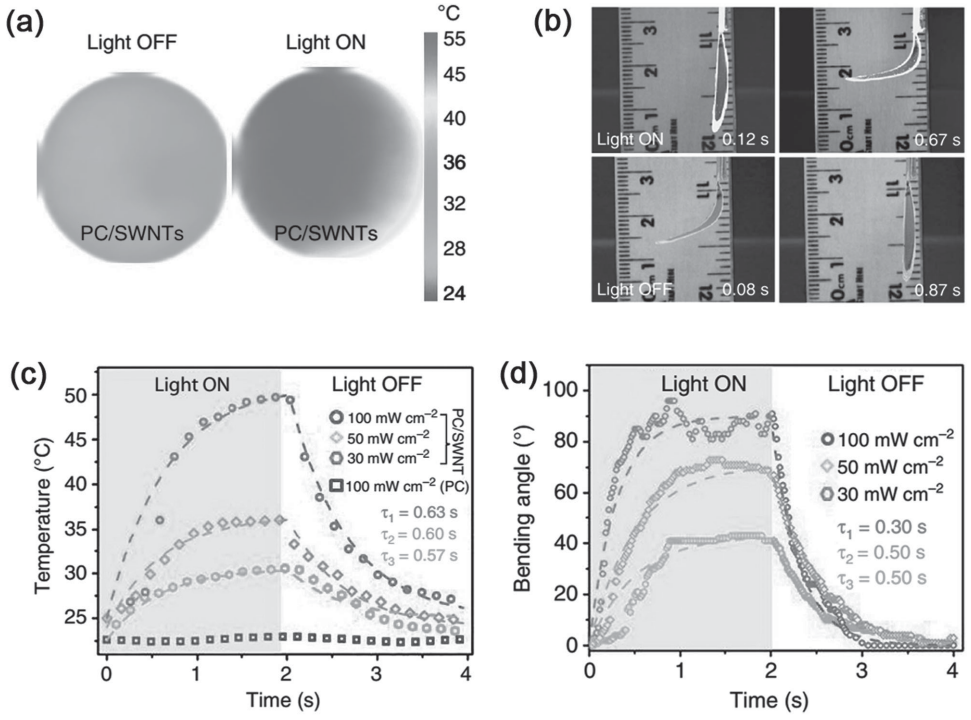

Figure 8. a) Infrared images of a PC/SWNT bilayer with and without light illumination. b) Series of optical images showing the light actuation process of a bilayer structure. c) Temperature measurements and d) bending angle of a PC/SWNT bilayer under different illumination intensities. Reproduced with permission.[29] Copyright 2014, Nature Publishing Group.

of PC membrane is over 10× larger than that of SWNTs, the bilayer structure is curled towards the SWNT side upon light irradiation (Figure 8b). The PC/SWNT bilayer film is very sensitive to light irradiation, within 2 seconds; the local temperature could rise to ≈50 °C from room temperature, leading to a bending angle up to ≈80° under 100 mW cm^{-2} illumination (Figure 8c,d). To endow this photoactuators with wavelength-selective response, nanotubes with different chirality distributions have been employed as photothermal layer; and smart curtains and sunlight-driven motors have been successfully fabricated. According to this basic principle, humanoid robot based on graphene-chitosan/polyethylene bimorph photoactuators;[122] roller blinds, smart box, and crawler-type robot based on RGO-CNT/PDMS;[36] swimming fish based on PDMS-PDMS/graphene nanoplatelets composited layer,[37] have been successfully reported.

To realize a more precise control over the performance, photothermal materials could be patterned at desired position. For instance, Dickey et al., patterned black ink on thin polystyrene films (Shrink-Dinks).[124] The ink provides localized absorption of light, which leads to a rapid local temperature rise of the polymer film underneath, and causes an origami-like folding, such as rectangular box and tetrahedral box. In this way, 2D planar structures could be converted into 3D structures under light irradiation. In addition to the patterning of photothermal materials, patterned light from a laser can also induce more complex deformation. To achieve arbitrary and fully reprogrammable patterns of local deformation within a single hydrogel sheet, Hauser et al., developed a controllable photothermal patterning gel by incorporating gold nanoparticles (AuNPs) into thermal deswelling poly(Nisopropylacrylamide-co-acrylic acid) hydrogel network.[39] With the help of surface plasmon resonance absorption of dispersed AuNPs and patterned illumination with visible light, rapid and localized photothermal deformation occurs only in the illuminated regions due to steady-state temperature gradients that can be understood by classical heat conduction equations. In this way, an almost limitless number of 3D shapes, for intance, a "bottle-like" shape, a helical roll, a dome-like elliptic surface, and a wrinkled hyperbolic surface, can easily be achieved from a single sheet. Importantly, the response time is dominated by poroelastic mass transport, rather than photochemical switching kinetics. Thus the reconfiguration of the macroscopic hydrogel sheets only needs several seconds. In fact, the response time could be further decreased when the hydrogel was shaped at micro- or nanoscale, while in that case, considerable difficulties would arise in the patterning of the light field. Notably, this method opens up the possibility of programmable control over the 3D configuration by changing the pattern of light.

In addition to photothermal expansion, photothermal effect induced molecular absorption/desorption that can lead to obvious volume change, also enable smart actuation. As a typical example, Mu et al., reported a graphene actuator with an asymmetric GO-polydopamine/RGO (GO-PDA/RGO) structure in response to environmental light.[71] In moisture, water molecules could be selectively adsorbed in GO-PDA regions; whereas under NIR light irradiation, the photothermal effect in the RGO regions induced a significant desorption of water

in the GO-PDA layer. In this way, the volume of the GO-PDA region could be controllably altered, and reversible bending deformation could be realized due to the interfacial stress. Based on this principle, an artificial hand made of such graphene paper has been demonstrated, it can hold an object five times heavier than itself.

3.3.2. Photothermal Effect Induced Phase Transition

Photothermal effect induced phase transition can be used to manipulate actuators. Some typical examples are shape memory polymers (SMPs),[41] LCEs,[125] and vanadium dioxide (VO_2) *etc.*[44,123] SMPs are a group of materials that that can memorize one or two temporary shapes and are able to return to their permanent shape upon exposure to an external stimulus such as heat, light, or magnetic field. As a typical SMP, Nafion shows tunable multishape memory effect with a broad thermal transition, since it possesses a broad glass transition from ≈55 °C to ≈130 °C. Generally, SMPs are deformed at a deformation temperature (T_d) and the deformed temporary shape is fixed upon cooling. When heated to a recovery temperature (T_r), the permanent shape could be recovered. The shape memory effect can be quantified on the basis of the percentage of shape fixation (R_f) and shape recovery (R_r), according to the following equations:[127]

$$R_f = 100\% \times \varepsilon/\varepsilon_{load} \quad (1)$$

$$R_r = 100\% \times (\varepsilon - \varepsilon_{rec})/\varepsilon \quad (2)$$

where ε_{load} represents the maximum strain under load, ε is the fixed strain after cooling and load removal, and ε_{rec} is the strain after recovery. The combination of SMPs with light-heat conversion materials makes it possible to fabricate phototermal actuators. Kohlmeyer et al., developed SWNT-Nafion composites,[41] in which the SWNTs can efficiently absorb and transform NIR light into thermal energy, thereby serving as numerous nanoscale heaters uniformly embedded in the Nafion matrix. Due to the photothermal phase transition, molecular mobility could be reversibly switched between two stable chemical states, leading to controllable photoactuation.

Unlike SMPs, LCEs are shape-changing polymers, which can reversibly switch shapes in response to an external stimulus, such as light, without the need of external mechanical manipulation. Kohlmeyer et al., make use of the photothermal N-I phase transition of LCE and demonstrated IR light-driven actuators based on SWNT-LCE/silicone bilayer film.[125] To endow this kind of photoactuators with wavelength specificity, NIR dyes with absorption wavelength between 980 nm and 1342 nm could be doped as fillers for the development of IR wavelength-selective actuators.

Besides organic SMPs and LC, inorganic VO_2 that undergoes a photothermal induced solid-solid phase transition also enable photothermal actuation by coupling VO_2 with an inactive material to form a bilayer structures. Since VO_2 goes through a fully reversible crystal structure transformation between a monoclinic phase and a tetragonal phase under external stimulations (e.g., temperature), abrupt change in area of the crystallographic planes would produce stress levels that generate significant actuation displacements. Moreover, the relative low phase transition temperature of VO_2 (~68 °C) gives the feasibility of manufacturing VO_2-based photothermal actuators with low power consumption. To further improve the light absorption, Wang et al., developed a cantilever photoactuator based on a SWNT/VO_2 bilayer structure (**Figure 9**).[44] The patterning of SWNT film was realized using oxygen plasma treatment, while the VO_2 layer was patterned using reactive ion etching. In their work, both bare VO_2 and SWNT/VO_2 bilayer cantilevers have been fabricated (Figure 9b). The presence of SWNT thin films significantly increases the photothermal efficiency, speed and responsivity of VO_2-based actuators (Figure 9c,d). The faster response of the SWNT/VO_2-based actuator can be clearly noticed. The light intensity used for Figure 9c is large enough to enter the phase transition for both bare VO_2 and SWNT/VO_2 bilayer devices. While if a slightly lower laser intensity is used, the bare VO_2 device does not even reach the beginning of the phase transition, thereby exhibiting only downward displacement (Figure 9d).

In addition to photothermal expansion and phase transition, there also exist some other photothermal effects that

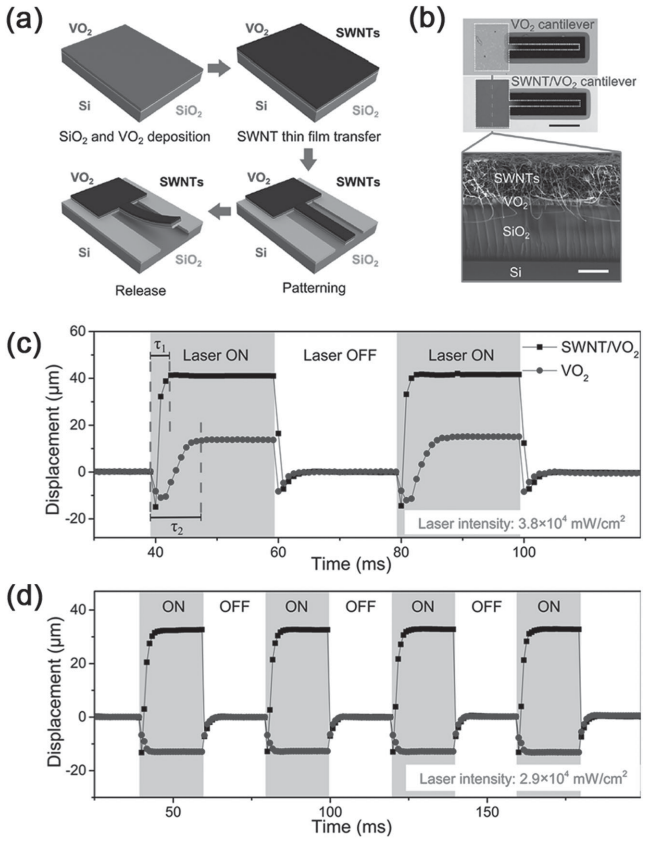

Figure 9. a) Fabrication process of SWNT/VO_2-based cantilever actuator. b) Top view photographs of VO_2 and SWNT/VO_2-based cantilevers. Scale bars: 200 μm. The zoomed image is a cross section SEM image of the SWNT/VO_2-based cantilever. Scale bars: 500 nm. c,d) Dynamic performance of the VO_2 and SWNT/VO_2-based cantilevers with driven laser intensity of 3.8×10^4 mW cm^{-2} and 2.9×10^4 mW cm^{-2}. Reproduced with permission.[44] Copyright 2015, American Chemical Society.

enable controllable manipulation. For instance, light-to-work conversion could be directly realized by photothermal surface tension effect, also known as Marangoni effect.[28,40,126] However, since the driving mechanism does not fit the scope of "actuator", details of this part of contents have not been included in this progress report. Actually, the essence of photothermal actuators lies in the development of photothermal materials that can convert light to heat effectively. Currently, the most popular photothermal material is CNT and SWNT due to their excellent light absorption property, mechanical strength, light weight and good stability. However, as a new member of carbon material family, graphene has not been involved in this field yet; possible reason would be the limitation in mass production. With the rapid progress of graphene preparation methodology (e.g., solvent exfoliation, chemical vapor deposition growth), we deem that graphene may find broad applications in actuators based on photothermal effects. To make an overview of light-mediated manipulation of actuators, typical works in this field have been summarized in **Table 2**.

4. Conclusion and Outlook

In this progress report, we summarized the recent development of actuators from the viewpoints of both light-mediated manufacture and light manipulation. In the former case, light-mediated processes have revealed great potential for designable fabrication of actuators based on a wide range of materials. In the latter case, light-mediated driven strategies, for instance, optical force actuation, photochemical actuation, and photothermal effect actuation have been well employed for manipulation of actuators. As a processing tool, light-mediated fabrication advantages designable construction of actuators profiles and tunable modification of materials properties. Meanwhile, as a neat and safe energy source, light enables controllable manipulation of actuators through a non-contact, wireless and effective manner. Obviously, light has emerged as a powerful tool for smart robots.

Although it has already achieved a great success in light-mediated manufacture and manipulation of actuators, there is still a large space for developing new photochemical/photophysical

Table 2. Typical examples of light manipulation of actuators.

Strategies	Mechanism	Materials	Actuation	Ref
Optical force	Optical tweezers	Photopolymer	μ-oscillator	[78]
	Angular momentum	Birefringent vaterite particle	Spinning	[4]
		Isotropic dielectric microparticles	Trapping/rotating	[73]
		Photoresist	micro-rotor	[80]
Photochemical routes	Photoisomerization	Azobenzene and derivatives	Bending/twisting/flexure/rolling	[3,11,33,99,105]
		Diarylethene and derivatives	Bending, twisting	[87,88]
		CLCPs using upconversion materials[a)]	Bending	[115,116]
		Spiropyran and derivatives	Valves, surface topography	[93]
	Photodimerization	9-Methylanthracene	Bending/twisting	[69]
		DMAAM[b)]	Curling	[89]
		9-Anthracene carboxylic acid	Bending, twisting	[90,91]
	photochemical reactions	NBA-integrated bilayer gels[c)]	Bending/palm	[14]
		Photoresist and surfactant	Direction control	[42]
Photothermal routes	Expansion/Contraction	Polymer/SWNT[d)]	Bending	[29]
		Graphene–chitosan/PE[e)]	Bending	[122]
		RGO–CNT/PDMS[f)]	Bending/folding	[36]
		Gradient porous hydrogels	Bending	[38]
		Shrinky-Dinks/polymer	Folding	[124]
		Hydrogel containing AuNPs[g)]	3D buckled shapes	[39]
		GO-PDA/RGO	Bending/folding	[71]
	Surface tension gradient	VANT-PDMS[h)]	Linear motion/rotor	[40]
		SU-8 with amorphous carbon	Rotating	[28]
	Phase transition	CNT–Nafion composites	Bending/coiling	[41]
		SWNT–LCE/silicone	Bending/folding	[125]
		SWNT/VO_2	Bending	[44]
		Cr/VO_2	Palm	[123]

[a)]Cross-linked liquid-crystal polymers using upconversion materials; [b)]Dimethyl-2(3-(anthracen-9-yl)allylidene)malonate; [c)]*o*-nitrobenzaldehyde-integrated bilayer gels; [d)]Polymer/single-walled carbon nanotube; [e)]Graphene-chitosan/polyethylene; [f)]Reduced graphene oxide-carbon nanotube/poly(dimethylsiloxane); [g)]Hydrogel containing gold nanoparticles; [h)]Vertically aligned carbon nanotube forests-polydimethylsiloxane.

schemes for innovative actuators. For instance, light-mediated actuator fabrication is currently limited to a few photosensitive materials, such as photoresists, hydrogel and GO; many smart materials that have certain response to external stimulus have not been involved in light-mediated processing. Additionally, despite some 2D patterns prepared through UV lithography show 3D reconfiguration under certain stimulation, direct 3D manufacture of actuators are still rare. In this regard, FsLDW technology that does not need shadow masks may demonstrate its full potential in programmable fabrication of 3D micro-actuators; in that way, more complex performance beyond bending, curling and twisting would be expected. In the case of light-mediated manipulation of actuators, photothermal effect induced expansion/contraction and even phase transition make it possible to fabricate various photo-responsive actuators based on a light-heat conversion process. Since the efficiency mainly depends on materials, the breakthrough on photothermal material may push forward the rapid development of photothermal actuators. However, the ambient temperature inevitably influences the manipulation of this kind of actuators. From this point of view, actuators based on photochemical response would be better choice if the ambient temperature is changeful.

As a generalisation, light plays a very important role in both manufacture and manipulation of actuators. In recent years, with the rapid progress of digital light processing technology and the innovation in photosensitive materials, light would become more and more popular in the development of actuators. We anticipate that light-mediated manufacture and manipulation methodology may pave the way for facile fabrication and operation of actuators.

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[1] D. D. Han, Y. L. Zhang, H. B. Jiang, H. Xia, J. Feng, Q. D. Chen, H. L. Xu, H. B. Sun, *Adv. Mater.* **2015**, *27*, 332.
[2] N. W. Bartlett, M. T. Tolley, J. T. B. Overvelde, J. C. Weaver, B. Mosadegh, K. Bertoldi, G. M. Whitesides, R. J. Wood, *Science* **2015**, *349*, 161.
[3] S. Iamsaard, S. J. Asshoff, B. Matt, T. Kudernac, J. Cornelissen, S. P. Fletcher, N. Katsonis, *Nat. Chem.* **2014**, *6*, 229.
[4] T. Wu, T. A. Nieminen, S. Mohanty, J. Miotke, R. L. Meyer, H. Rubinsztein-Dunlop, M. W. Berns, *Nat. Photonics* **2012**, *6*, 62.
[5] J. L. Silverberg, J. H. Na, A. A. Evans, B. Liu, T. C. Hull, C. D. Santangelo, R. J. Lang, R. C. Hayward, I. Cohen, *Nat. Mater.* **2015**, *14*, 389.
[6] J. H. Son, B. Cho, S. Hong, S. H. Lee, O. Hoxha, A. J. Haack, L. P. Lee, *Light: Sci. Appl.* **2015**, *4*, 7.
[7] O. M. Marago, P. H. Jones, P. G. Gucciardi, G. Volpe, A. C. Ferrari, *Nat. Nanotechnol.* **2013**, *8*, 807.
[8] Y. L. Sun, W. F. Dong, L. G. Niu, T. Jiang, D. X. Liu, L. Zhang, Y. S. Wang, Q. D. Chen, D. P. Kim, H. B. Sun, *Light: Sci. Appl.* **2014**, *3*, 7.
[9] a) Y. D. Han, Y. B. Lee, S. Park, S. Jeon, A. J. Epstein, J. H. Kim, J. Kim, K. S. Lee, J. Joo, *NPG Asia Mater.* **2014**, *6*, 9; b) K. Ariga, J. B. Li, J. B. Fei, Q. M. Ji, J. P. Hill, *Adv. Mater.* **2016**, *28*, 1251; c) K. Ariga, Q. Ji, J. P. Hill, Y. Bando, M. Aono, *NPG Asia Mater.* **2012**, *4*, e17; d) K. Lee, Y. Cui, L. P. Lee, J. Irudayaraj, *Nat. Nanotechnol.* **2014**, *9*, 474.
[10] K. Malachowski, M. Jamal, Q. R. Jin, B. Polat, C. J. Morris, D. H. Gracias, *Nano Lett.* **2014**, *14*, 4164.
[11] S. F. Guo, K. Matsukawa, T. Miyata, T. Okubo, K. Kuroda, A. Shimojima, *J. Am. Chem. Soc.* **2015**, *137*, 15434.
[12] M. Irie, T. Fulcaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174.
[13] J. Kim, J. A. Hanna, M. Byun, C. D. Santangelo, R. C. Hayward, *Science* **2012**, *335*, 1201.
[14] P. Techawanitchai, M. Ebara, N. Idota, T. A. Asoh, A. Kikuchi, T. Aoyagi, *Soft Matter* **2012**, *8*, 2844.
[15] J. Zhang, L. Song, Z. Zhang, N. Chen, L. Qu, *Small* **2014**, *10*, 2151.
[16] a) W. Nakanishi, K. Minami, L. K. Shrestha, Q. M. Ji, J. P. Hill, K. Ariga, *Nano Today* **2014**, *9*, 378; b) G. Rydzek, Q. M. Ji, M. Li, P. Schaaf, J. P. Hill, F. Boulmedais, K. Ariga, *Nano Today* **2015**, *10*, 138; c) K. Ariga, T. Mori, J. P. Hill, *Adv. Mater.* **2012**, *24*, 158; d) K. Sakakibara, J. P. Hill, K. Ariga, *Small* **2011**, *7*, 1288; e) Q. Sun, K. Ueno, H. Yu, A. Kubo, Y. Matsuo, H. Misawa, *Light: Sci. Appl.* **2013**, *2*, 8; f) A. S. Gladman, E. A. Matsumoto, R. G. Nuzzo, L. Mahadevan, J. A. Lewis, *Nat. Mater.* **2016**, *15*, 413.
[17] a) D. Yang, B. Mosadegh, A. Ainla, B. Lee, F. Khashai, Z. G. Suo, K. Bertoldi, G. M. Whitesides, *Adv. Mater.* **2015**, *27*, 6323; b) F. M. Qiu, S. Fujita, R. Mhanna, L. Zhang, B. R. Simona, B. J. Nelson, *Adv. Funct. Mater.* **2015**, *25*, 1666; c) J. C. Ndukaife, A. V. Kildishev, A. G. A. Nnanna, V. M. Shalaev, S. T. Wereley, A. Boltasseva, *Nat. Nanotechnol.* **2016**, *11*, 53; d) K. Ueno, H. Misawa, *NPG Asia Mater.* **2013**, *5*, 6.
[18] D. Y. Chen, J. Yoon, D. Chandra, A. J. Crosby, R. C. Hayward, *J. Polym. Sci., Part B: Polym. Phys.s* **2014**, *52*, 1441.
[19] H. Xia, J. A. Wang, Y. Tian, Q. D. Chen, X. B. Du, Y. L. Zhang, Y. He, H. B. Sun, *Adv. Mater.* **2010**, *22*, 3204.
[20] A. Lehmuskero, P. Johansson, H. Rubinsztein-Dunlop, L. M. Tong, M. Kall, *ACS Nano* **2015**, *9*, 3453.
[21] D. Palima, J. Gluckstad, *Laser Photonics Rev.* **2013**, *7*, 478.
[22] M. Jamal, A. M. Zarafshar, D. H. Gracias, *Nat. Commun.* **2011**, *2*, 6.
[23] Y. L. Sun, Q. Li, S. M. Sun, J. C. Huang, B. Y. Zheng, Q. D. Chen, Z. Z. Shao, H. B. Sun, *Nat. Commun.* **2015**, *6*, 10.
[24] H. H. Cheng, J. Liu, Y. Zhao, C. G. Hu, Z. P. Zhang, N. Chen, L. Jiang, L. T. Qu, *Angew. Chem. Int. Ed.* **2013**, *52*, 10482.
[25] a) R. Krini, C. W. Ha, P. Prabhakaran, H. El Mard, D. Y. Yang, R. Zentel, K. S. Lee, *Macromol. Rapid Commun.* **2015**, *36*, 1108; b) W. Xiong, Y. S. Zhou, W. J. Hou, L. J. Jiang, Y. Gao, L. S. Fan, L. Jiang, J. F. Silvain, Y. F. Lu, *Sci. Rep.* **2014**, *4*, 6; c) D. Li, W. Xiong, L. Jiang, Z. Xiao, H. R. Golgir, M. Wang, X. Huang, Y. Zhou, Z. Lin, J. Song, S. Ducharme, L. Jiang, J.-F. Silvain, Y. Lu, *ACS Nano* **2016**, *10*, 3766; d) J. H. Cho, M. D. Keung, N. Verellen, L. Lagae, V. V. Moshchalkov, P. V. Dorpe, D. H. Gracias, *Small* **2011**, *14*, 1943.
[26] C. L. Randall, E. Gultepe, D. H. Gracias, *Trends Biotechnol.* **2012**, *30*, 138.
[27] Y. L. Sun, W. F. Dong, R. Z. Yang, X. Meng, L. Zhang, Q. D. Chen, H. B. Sun, *Angew. Chem. Int. Ed.* **2012**, *51*, 1558.
[28] C. Maggi, F. Saglimbeni, M. Dipalo, F. De Angelis, R. Di Leonardo, *Nat. Commun.* **2015**, *6*, 5.
[29] X. Zhang, Z. B. Yu, C. Wang, D. Zarrouk, J. W. T. Seo, J. C. Cheng, A. D. Buchan, K. Takei, Y. Zhao, J. W. Ager, J. J. Zhang, M. Hettick,

M. C. Hersam, A. P. Pisano, R. S. Fearing, A. Javey, *Nat. Commun.* **2014**, *5*, 8.
[30] C. L. van Oosten, C. W. M. Bastiaansen, D. J. Broer, *Nat. Mater.* **2009**, *8*, 677.
[31] X. B. Zhang, C. L. Pint, M. H. Lee, B. E. Schubert, A. Jamshidi, K. Takei, H. Ko, A. Gillies, R. Bardhan, J. J. Urban, M. Wu, R. Fearing, A. Javey, *Nano Lett.* **2011**, *11*, 3239.
[32] S. Hong, M. Y. Lee, A. O. Jackson, L. P. Lee, *Light: Sci. Appl.* **2015**, *4*, 7.
[33] Y. L. Yu, M. Nakano, T. Ikeda, *Nature* **2003**, *425*, 145.
[34] H. F. Yu, T. Ikeda, *Adv. Mater.* **2011**, *23*, 2149.
[35] J. E. Stumpel, D. J. Broer, A. Schenning, *Chem. Commun.* **2014**, *50*, 15839.
[36] Y. Hu, G. Wu, T. Lan, J. J. Zhao, Y. Liu, W. Chen, *Adv. Mater.* **2015**, *27*, 7867.
[37] W. T. Jiang, D. Niu, H. Z. Liu, C. H. Wang, T. T. Zhao, L. Yin, Y. S. Shi, B. D. Chen, Y. C. Ding, B. H. Lu, *Adv. Funct. Mater.* **2014**, *24*, 7598.
[38] R. C. Luo, J. Wu, N. D. Dinh, C. H. Chen, *Adv. Funct. Mater.* **2015**, *25*, 7272.
[39] A. W. Hauser, A. A. Evans, J. H. Na, R. C. Hayward, *Angew. Chem. Int. Ed.* **2015**, *54*, 5434.
[40] D. Okawa, S. J. Pastine, A. Zettl, J. M. J. Frechet, *J. Am. Chem. Soc.* **2009**, *131*, 5396.
[41] R. R. Kohlmeyer, M. Lor, J. Chen, *Nano Lett.* **2012**, *12*, 2757.
[42] M. Xiao, C. Jiang, F. Shi, *NPG Asia Mater.* **2014**, *6*, e128.
[43] N. K. Nath, L. Pejov, S. M. Nichols, C. H. Hu, N. Saleh, B. Kahr, P. Naumov, *J. Am. Chem. Soc.* **2014**, *136*, 2757.
[44] T. Y. Wang, D. Torres, F. E. Fernandez, A. J. Green, C. Wang, N. Sepulveda, *ACS Nano* **2015**, *9*, 4371.
[45] J. H. Na, A. A. Evans, J. Bae, M. C. Chiappelli, C. D. Santangelo, R. J. Lang, T. C. Hull, R. C. Hayward, *Adv. Mater.* **2015**, *27*, 79.
[46] D. D. Han, Y. L. Zhang, Y. Liu, Y. Q. Liu, H. B. Jiang, B. Han, X. Y. Fu, H. Ding, H. L. Xu, H. B. Sun, *Adv. Funct. Mater.* **2015**, *25*, 4548.
[47] Y. L. Zhang, Q. D. Chen, H. Xia, H. B. Sun, *Nano Today* **2010**, *5*, 435.
[48] T. Kamal, S. Y. Park, *ACS Appl. Mater. Interfaces* **2014**, *6*, 18048.
[49] J. Ryu, M. D'Amato, X. D. Cui, K. N. Long, H. J. Qi, M. L. Dunn, *Appl. Phys. Lett.* **2012**, *100*, 5.
[50] L. T. de Haan, V. Gimenez-Pinto, A. Konya, T. S. Nguyen, J. M. N. Verjans, C. Sanchez-Somolinos, J. V. Selinger, R. L. B. Selinger, D. J. Broer, A. Schenning, *Adv. Funct. Mater.* **2014**, *24*, 1251.
[51] E. Gultepe, J. S. Randhawa, S. Kadam, S. Yamanaka, F. M. Selaru, E. J. Shin, A. N. Kalloo, D. H. Gracias, *Adv. Mater.* **2013**, *25*, 514.
[52] T. Kamal, S. Y. Park, *Chem. Commun.* **2014**, *50*, 2030.
[53] N. Bassik, A. Brafman, A. M. Zarafshar, M. Jamal, D. Luvsanjav, F. M. Selaru, D. H. Gracias, *J. Am. Chem. Soc.* **2010**, *132*, 16314.
[54] K. Ariga, Q. M. Ji, T. Mori, M. Naito, Y. Yamauchi, H. Abe, J. P. Hill, *Chem. Soc. Rev.* **2013**, *42*, 6322.
[55] a) J. Kim, J. A. Hanna, R. C. Hayward, C. D. Santangelo, *Soft Matter* **2012**, *8*, 2375; b) M. Byun, C. D. Santangelo, R. C. Hayward, *Soft Matter* **2013**, *9*, 8264.
[56] T. Deng, C. Yoon, Q. R. Jin, M. G. Li, Z. W. Liu, D. H. Gracias, *Appl. Phys. Lett.* **2015**, *106*, 4.
[57] S. Tottori, L. Zhang, F. M. Qiu, K. K. Krawczyk, A. Franco-Obregon, B. J. Nelson, *Adv. Mater.* **2012**, *24*, 811.
[58] D. X. Liu, Y. L. Sun, W. F. Dong, R. Z. Yang, Q. D. Chen, H. B. Sun, *Laser Photonics Rev.* **2014**, *8*, 882.
[59] Y. L. Zhang, L. Guo, H. Xia, Q. D. Chen, J. Feng, H. B. Sun, *Adv. Opt. Mater.* **2014**, *2*, 10.
[60] Y. Zhang, L. Guo, S. Wei, Y. He, H. Xia, Q. Chen, H.-B. Sun, F.-S. Xiao, *Nano Today* **2010**, *5*, 15.
[61] B. B. Xu, L. Wang, Z. C. Ma, R. Zhang, Q. D. Chen, C. Lv, B. Han, X. Z. Xiao, X. L. Zhang, Y. L. Zhang, K. Ueno, H. Misawa, H. B. Sun, *ACS Nano* **2014**, *8*, 6682.
[62] B. B. Xu, Y. L. Zhang, R. Zhang, L. Wang, X. Z. Xiao, H. Xia, Q. D. Chen, H. B. Sun, *J. Mater. Chem. C* **2013**, *1*, 4699.
[63] M. R. Lee, I. Y. Phang, Y. Cui, Y. H. Lee, X. Y. Ling, *Small* **2015**, *11*, 740.
[64] Y. Tian, Y.-L. Zhang, H. Xia, L. Guo, J.-F. Ku, Y. He, R. Zhang, B.-Z. Xu, Q.-D. Chen, H.-B. Sun, *Phys. Chem. Chem. Phys.* **2011**, *13*, 4835.
[65] D. X. Lu, Y. L. Zhang, D. D. Han, H. Wang, H. Xia, Q. D. Chen, H. Ding, H. B. Sun, *J. Mater. Chem. C* **2015**, *3*, 1751.
[66] K. Dholakia, P. Reece, *Nano Today* **2006**, *1*, 18.
[67] X. F. Fan, W. T. Zheng, D. J. Singh, *Light: Sci. Appl.* **2014**, *3*, 14.
[68] M. Camacho-Lopez, H. Finkelmann, P. Palffy-Muhoray, M. Shelley, *Nat. Mater.* **2004**, *3*, 307.
[69] T. Kim, L. C. Zhu, L. J. Mueller, C. J. Bardeen, *J. Am. Chem. Soc.* **2014**, *136*, 6617.
[70] L. D. Zhang, H. R. Liang, J. Jacob, P. Naumov, *Nat. Commun.* **2015**, *6*, 11.
[71] J. Mu, C. Hou, H. Wang, Y. Li, Q. Zhang, M. Zhu, *Sci. Adv.* **2015**, *1*.
[72] A. Ashkin, *Phys. Rev. Lett.* **1970**, *24*, 156.
[73] W. Y. Tsai, J. S. Huang, C. B. Huang, *Nano Lett.* **2014**, *14*, 547.
[74] D. Van Thourhout, J. Roels, *Nat. Photonics* **2010**, *4*, 211.
[75] a) P. A. M. Neto, H. M. Nussenzveig, *Europhys. Lett.* **2000**, *50*, 702; b) A. Ashkin, *Biophys. J.* **1992**, *61*, 569; c) A. B. Stilgoe, T. A. Nieminen, G. Knoner, N. R. Heckenberg, H. Rubinsztein-Dunlop, *Opt. Express* **2008**, *16*, 15039.
[76] a) K. Svoboda, S. M. Block, *Opt. Lett.* **1994**, *19*, 930; b) T. Cizmar, L. C. D. Romero, K. Dholakia, D. L. Andrews, *J. Phys. B: At., Mol. Opt. Phys.* **2010**, *43*, 25; c) M. Daly, M. Sergides, S. N. Chormaic, *Laser Photonics Rev.* **2015**, *9*, 309.
[77] a) J. Liesener, M. Reicherter, T. Haist, H. J. Tiziani, *Opt. Commun.* **2000**, *185*, 77; b) J. E. Curtis, B. A. Koss, D. G. Grier, *Opt. Commun.* **2002**, *207*, 169; c) G. Sinclair, P. Jordan, J. Courtial, M. Padgett, J. Cooper, Z. J. Laczik, *Opt. Express* **2004**, *12*, 5475; d) S. Nedev, A. S. Urban, A. A. Lutich, J. Feldmann, *Nano Lett.* **2011**, *11*, 5066.
[78] S. Kawata, H. B. Sun, T. Tanaka, K. Takada, *Nature* **2001**, *412*, 697.
[79] M. Padgett, R. Bowman, *Nat. Photonics* **2011**, *5*, 343.
[80] X. F. Lin, G. Q. Hu, Q. D. Chen, L. G. Niu, Q. S. Li, A. Ostendorf, H. B. Sun, *Appl. Phys. Lett.* **2012**, *101*, 4.
[81] a) T. J. White, *J. Polym. Sci., Part B: Polym. Phys.* **2012**, *50*, 877; b) L. T. de Haan, A. Schenning, D. J. Broer, *Polymer* **2014**, *55*, 5885; c) J. Wei, Y. L. Yu, *Soft Matter* **2012**, *8*, 8050; d) T. J. White, D. J. Broer, *Nat. Mater.* **2015**, *14*, 1087; e) D. J. Broer, C. M. W. Bastiaansen, M. G. Debije, A. Schenning, *Angew. Chem. Int. Ed.* **2012**, *51*, 7102.
[82] J. Cui, A. del Campo, in *Smart Polymers and their Applications*, Woodhead Publishing Limited, Cambridge, **2014**, 93.
[83] S. Y. Gao, K. Ueno, H. Misawa, *Acc. Chem. Res.* **2011**, *44*, 251.
[84] D. Q. Liu, L. Liu, P. R. Onck, D. J. Broer, *Proc. Natl. Acad. Sci. USA* **2015**, *112*, 3880.
[85] P. Palffy-Muhoray, *Nat. Mater.* **2009**, *8*, 614.
[86] S. Kobatake, S. Takami, H. Muto, T. Ishikawa, M. Irie, *Nature* **2007**, *446*, 778.
[87] F. Terao, M. Morimoto, M. Irie, *Angew. Chem. Int. Ed.* **2012**, *51*, 901.
[88] M. Morimoto, M. Irie, *J. Am. Chem. Soc.* **2010**, *132*, 14172.
[89] T. Kim, M. K. Al-Muhanna, S. D. Al-Suwaidan, R. O. Al-Kaysi, C. J. Bardeen, *Angew. Chem. Int. Ed.* **2013**, *52*, 6889.
[90] R. O. Al-Kaysi, C. J. Bardeen, *Adv. Mater.* **2007**, *19*, 1276.
[91] L. Y. Zhu, R. O. Al-Kaysi, C. J. Bardeen, *J. Am. Chem. Soc.* **2011**, *133*, 12569.

[92] a) H. Koshima, K. Takechi, H. Uchimoto, M. Shiro, D. Hashizume, *Chem. Commun.* **2011**, *47*, 11423; b) H. Koshima, R. Matsuo, M. Matsudomi, Y. Uemura, M. Shiro, *Cryst. Growth Des.* **2013**, *13*, 4330.
[93] a) J. ter Schiphorst, S. Coleman, J. E. Stumpel, A. Ben Azouz, D. Diamond, A. Schenning, *Chem. Mater.* **2015**, *27*, 5925; b) J. E. Stumpel, B. Ziolkowski, L. Florea, D. Diamond, D. J. Broer, A. Schenning, *ACS Appl. Mater. Interfaces* **2014**, *6*, 7268.
[94] R. Klajn, *Chem. Soc. Rev.* **2014**, *43*, 148.
[95] H. Shoji, D. Kitagawa, S. Kobatake, *New J. Chem.* **2014**, *38*, 933.
[96] F. Castet, V. Rodriguez, J. L. Pozzo, L. Ducasse, A. Plaquet, B. Champagne, *Acc. Chem. Res.* **2013**, *46*, 2656.
[97] X. Y. Zhang, L. L. Hou, P. Samori, *Nat. Commun.* **2016**, *7*, 14.
[98] D. Q. Liu, D. J. Broer, *Angew. Chem. Int. Ed.* **2014**, *53*, 4542.
[99] K. M. Lee, M. L. Smith, H. Koerner, N. Tabiryan, R. A. Vaia, T. J. Bunning, T. J. White, *Adv. Funct. Mater.* **2011**, *21*, 2913.
[100] J. A. Lv, W. Wang, W. Wu, Y. L. Yu, *J. Mater. Chem. C* **2015**, *3*, 6621.
[101] a) M. Yamada, M. Kondo, R. Miyasato, Y. Naka, J. Mamiya, M. Kinoshita, A. Shishido, Y. L. Yu, C. J. Barrett, T. Ikeda, *J. Mater. Chem.* **2009**, *19*, 60; b) M. Yamada, M. Kondo, J. I. Mamiya, Y. L. Yu, M. Kinoshita, C. J. Barrett, T. Ikeda, *Angew. Chem. Int. Ed.* **2008**, *47*, 4986.
[102] S. V. Serak, N. V. Tabiryan, T. J. White, T. J. Bunning, *Opt. Express* **2009**, *17*, 15736.
[103] S. Serak, N. Tabiryan, R. Vergara, T. J. White, R. A. Vaia, T. J. Bunning, *Soft Matter* **2010**, *6*, 779.
[104] R. Tang, Z. Y. Liu, D. D. Xu, J. Liu, L. Yu, H. F. Yu, *ACS Appl. Mater. Interfaces* **2015**, *7*, 8393.
[105] H. Y. Wen, W. D. Zhang, Y. Y. Weng, Z. J. Hu, *RSC Adv.* **2014**, *4*, 11776.
[106] F. T. Cheng, R. Y. Yin, Y. Y. Zhang, C. C. Yen, Y. L. Yu, *Soft Matter* **2010**, *6*, 3447.
[107] M. L. Chen, H. T. Huang, Y. T. Zhu, Z. Liu, X. Xing, F. T. Cheng, Y. L. Yu, *Appl. Phys. A: Mater. Sci. Process.* **2011**, *102*, 667.
[108] Y. T. Zhu, L. H. Zheng, Z. Liu, H. Liu, Y. L. Yu, *Appl. Phys. A: Mater. Sci. Process.* **2014**, *115*, 1167.
[109] J. Lee, S. Oh, J. Pyo, J. M. Kim, J. H. Je, *Nanoscale* **2015**, *7*, 6457.
[110] D. Kitagawa, S. Kobatake, *Chem. Commun.* **2015**, *51*, 4421.
[111] a) L. D. Zhang, P. Naumov, *Angew. Chem. Int. Ed.* **2015**, *54*, 8642; b) T. Lan, W. Chen, *Angew. Chem. Int. Ed.* **2013**, *52*, 6496; c) M. Kondo, Y. L. Yu, T. Ikeda, *Angew. Chem. Int. Ed.* **2006**, *45*, 1378; d) H. F. Yu, C. Dong, W. M. Zhou, T. Kobayashi, H. A. Yang, *Small* **2011**, *7*, 3039.
[112] M. L. Smith, K. M. Lee, T. J. White, R. A. Vaia, *Soft Matter* **2014**, *10*, 1400.
[113] D. Kusano, R. Ohshima, N. Hosono, K. Totani, T. Watanabe, *Polymer* **2014**, *55*, 5648.
[114] L. Cheng, Y. Torres, K. M. Lee, A. J. McClung, J. Baur, T. J. White, W. S. Oates, *J. Appl. Phys.* **2012**, *112*, 16.
[115] Z. Jiang, M. Xu, F. Y. Li, Y. L. Yu, *J. Am. Chem. Soc.* **2013**, *135*, 16446.
[116] W. Wu, L. M. Yao, T. S. Yang, R. Y. Yin, F. Y. Li, Y. L. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 15810.
[117] R. Y. Yin, W. X. Xu, M. Kondo, C. C. Yen, J. Mamiya, T. Ikeda, Y. L. Yu, *J. Mater. Chem.* **2009**, *19*, 3141.
[118] T. Ozawa, M. Kondo, J. Mamiya, T. Ikeda, *J. Mater. Chem. C* **2014**, *2*, 2313.
[119] C. Q. Qin, Y. Y. Feng, W. Luo, C. Cao, W. P. Hu, W. Feng, *J. Mater. Chem. A* **2015**, *3*, 16453.
[120] T. Ube, K. Takado, T. Ikeda, *J. Mater. Chem. C* **2015**, *3*, 8006.
[121] W. Wang, X. M. Sun, W. Wu, H. S. Peng, Y. L. Yu, *Angew. Chem. Int. Ed.* **2012**, *51*, 4644.
[122] C. Z. Wu, J. Feng, L. L. Peng, Y. Ni, H. Y. Liang, L. H. He, Y. Xie, *J. Mater. Chem.* **2011**, *21*, 18584.
[123] K. Liu, C. Cheng, Z. T. Cheng, K. V. Wang, R. Ramesh, J. Q. Wu, *Nano Lett.* **2012**, *12*, 6302.
[124] Y. Liu, J. K. Boyles, J. Genzer, M. D. Dickey, *Soft Matter* **2012**, *8*, 1764.
[125] R. R. Kohlmeyer, J. Chen, *Angew. Chem. Int. Ed.* **2013**, *52*, 9234.
[126] G. L. Liu, J. Kim, Y. Lu, L. P. Lee, *Nat. Mater.* **2006**, *5*, 27.
[127] T. Xie, *Nature* **2010**, *464*, 267.